# Ion exchange separation of Chromium(III) complexes

"Green chromium chloride" is actually trans-dichlorotetraaquachromium(III) chloride dihydrate. It separates as green crystals from solutions of chromium(III) in hydrochloric acid. The salt is fairly soluble (almost 600 g in 1 litre of water) and the solution owes its green colour to the cation. The absorption spectrum of a solution of the salt in pure water is, however, not constant over time; the solution is therefore not in equilibrium, and the maxima in the spectrum gradually shifts to shorter wavelengths. This means that chloride is substituted by a ligand higher in the spectrochemical series, in case water. The green cation can be said to hydrolyse. The hydrolysis is slow, just as substitution reactions on chromium(III) are in general. The hydrolysis takes place in two steps according to

$$Cr(H_2O)_4Cl_2^+ + 2H_2O \leftrightarrows Cr(H_2O)_5Cl^{2+} + Cl^- + H_2O \leftrightarrows Cr(H_2O)_6^{3+} + 2\ Cl^-$$
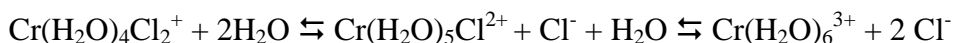
The two consecutive dissociation constants are 130 M and 16 M respectively.

The three chromium(III) complexes have different charges which make them very different with respect to electrostatic interactions with negatively charged particles. This is the fundamental principle behind the successful separation of different cations on a column of a ion exchange resin.

Ion exchange chromatography

An ion exchange resin is, in short, a solid polymer containing groups with negative charges on the surface. These negatively charged groups may be sulfonates, phosphonates or carboxylates attached to the polymer. Just as in clay minerals the negative charge of the ion exchange resin is neutralised by cations, which are more or less loosely attached to the negative surface, balancing the net charge to zero in the material. The force by which cations are bound to the polymer depends on the cation properties, mainly its size and the magnitude of its charge. In the ready-to-use resin the cation may be the proton (on sulphonate resins) or e.g. the sodium ion. These ions are only loosely attached to the negative groups and may therefore be substituted by other cations, which bind better. The first step is therefore to pour a solution containing a mixture of cations on the top of a column filled with the resin, which will take up the best binding cations first staying in the top layer of the material. Further down the column the less strongly binding cations bind in layers in order of decreasing binding strength.

In the present case the cation with three positive charges will bind first and the cations with a smaller charge will bind in lower layers. If all three of the above chromium complexes are present, the order of binding will be

$$Cr(H_2O)_6^{3+} > Cr(H_2O)_5Cl^{2+} > Cr(H_2O)_4Cl_2^+$$
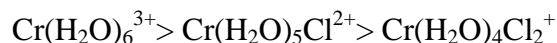
The second step is to take the ions off the resin. This is effected by the addition of acid of some concentration. The protons will compete with the three cations for the anionic sites on the resin and since the $Cr(H_2O)_4Cl_2^+$ with only one charge is the weakest bonded cation, it is substituted by protons first. This competition can be expressed by the following scheme

$$cation_{resin} + H^+_{aq} \leftrightarrows cation_{aq} + H^+_{resin}$$
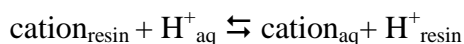
It is obvious, that the larger the acidity of the solution the more is the equilibrium shifted to the right.

In the present case, when an acid of a certain concentration is passed through a column of the resin with the three different cations attached to the negative sites of the resin, the $Cr(H_2O)_4Cl_2^+$ can be liberated to the solution, while the two other cations stick to it. This leaves a solution with only $Cr(H_2O)_4Cl_2^+$ ions (plus acid) and the two other cations remaining on the column in two layers. Now, if the acid concentration is raised it is $Cr(H_2O)_5Cl^{2+}$, which is the next cation to loose the competition to the protons for the negative sites on the resin. $Cr(H_2O)_5Cl^{2+}$ will accordingly be liberated to the acid solution. The hexaaqua-chromium(III) ion with its three charges will only be oust by protons if the acid concentration is raised further.

The principle of ion exchange between sites on a stationary phase an a bypassing solution is called ion exchange chromatography. The principle finds wide spread use to separate mixtures and isolate pure compounds, and is also operating in soil where clay minerals and humus bind cations in equilibrium with the soil solution, taken up by plants.

In this experiment the commercial salt "green chromium chloride" is used as a starting material for the preparation of the two products of hydrolysis and the purity of the three complex cations brought about by the use of cation exchange chromatography. This serves as a way to record absorption spectra of the pure compounds.

Experimental procedure

Safety note: perchloric acid is an oxidising agent, which - when pure - can react vigorously with organic matter and other reducing agents. The reactions normally need some activation to proceed and may then react in a self speeding reaction, an explosion. The concentrations of perchloric acid used here are safe to handle when precaution is taken to keep them away from organic compounds and reducing agents.
Solutions of perchloric acid and chromium(III) are collected in a labelled container for further waste management.

Preparation of Ion Exchange Column
Prepare around 15 ml of slurry of the resin Dowex 50W-X8 (50-100 mesh, H^+-form) and pour it slowly but steady into a buret (Ø ~1 cm), which is filled with deionised water and equipped with a plug of glass wool near the open stopcock. The drips of liquid are continuously collected in a beaker below the column. When all the slurry has been added, a 5 mm layer of see sand is added (in a water slurry) onto the top of the resin. The see sand is denser than the resin and helps avoiding the upper layer of the resin to be whirled up when aqueous solutions are added to the top of the column. After having allowed enough water to pass through the column to leave the effluent colourless, the column is ready for use. Be sure, that the see sand is always covered by 1 cm of liquid to avoid it being partly drained out leaving channels and irregularity - the column should be as homogenous as possible to give the best separation.

trans-Dichlorotetraaquachromium(III)
Weigh out 2.35 g (8.8 mmol) of "green chromium chloride" to make a 0.35 M stock solution of chromium(III) in 2 ml of 0.1 M perchloric acid and water in a 25 ml measuring flask. Record the time of dissolution and keep the solution at room temperature.
Add 5 ml of the stock solution to the cation exchange column and open the buret stopcock to allow the liquid sink through the column. When the surface just above the top of the see sand layer, pour on 0.1 M perchloric acid, which acts as an eluent. The green colour is seen to

move down the column, and the most intensely coloured green portion is colleted, when it drips out of the buret. Collect at least 5 ml for the recording of an absorption spectrum (800 - 350 nm), using a cuvettes of OS or QS quality, and 0.1 M perchloric acid as the reference.

Chloropentaaquachromium(III)
The dichlortetraaquachromium(III) when heated shortly is hydrolysed to chloropentaaqua-chromium(III). Heat 5 ml of the stock solution in an conical flask in a water bath (~ 100 ^{o}C) for 3 minutes. Now add 5 ml of deionised water and pour the now cooled solution into the buret as in the first experiment. First flush with 0.1 m perchloric acid to remove the unreacted dichlorotetraaquachromium(III). Next elute with 1.0 M perchloric acid to get out and collect 5 ml of the most intensely coloured fraction of chloropentaaquachromium(III) in the same way as before. Record a spectrum as specified above.

Hexaaquachromium(III)
Boil a mixture of 5 ml of the stock solution and 5 ml of deionised water for 5 minutes, and add the solution to the buret as above. Use sufficient 1.0 M perchloric to get the unreacted complexes out and then elute with 4.0 M perchloric acid. Again collect 5 ml of the most intensely coloured fraction of hexaaquachromium(III) and record the spectrum as specified above.

Report

Report the recorded visible absorption spectra of the three chromium complexes in question. Characterise each spectrum by values of $(\lambda,A)_{max}$ and $(\lambda,A)_{min}$, A being the observed absorbance at the extrema.
Comment on the validity of the average environment rule used in this case using both sets of maxima.
What would have been the overall result if hydrochloric, instead of perchloric acid, had been used throughout the experiments.